91602
new 82-10

COMPLIMENTARY COPY
Please Credit Ontario Hydro Research If
Reproduced in Whole or in Part

ontario hydro
research division

To: Dr. D. Mills
Director of Research

The Normalization of Heavy Water Enriched in Oxygen-18 For Use in Nutritional Studies

Jeffrey R. Robins

Diagnostic tests for nutritional studies require water enriched in oxygen-18, but not in deuterium. Water distillation, the best method for producing oxygen-18, enriches deuterium along with the oxygen. Therefore production facilities need methods to replace the deuterium with hydrogen. This report examines two such methods, electrolysis and recombination, and direct hydrogen exchange.

1.0 Introduction

One of the emerging technologies making use of oxygen 18 is the application of "double labelled water ($D_2{}^{18}O$)" as a method of measuring energy expenditure in humans /1/. Total energy expenditure can be computed from carbon dioxide production. The technique assesses this carbon dioxide production by measuring the disappearance of deuterium and oxygen-18 in urine samples taken after an oral dose of these tracers has been given to the patient. This technique is the first genuinely non-invasive method for measuring energy expenditure in free-living people and provides estimates of habitual expenditure over a time period of 10-20 days. It is safe and user-friendly for the subjects, because it does not require them to do anything except provide regular urine samples.

The technique has been applied to premature babies, infants, children, pregnant women, normal and obese adults, athletes, hospitalized patients and the elderly. Canadian nutritionalists are applying these methods to the energy expenditure of

job	file	date	report no.
16-682	819.43	May 14, 1991	91-115-K

LEGAL NOTICE

This report was prepared by Ontario Hydro and, while effort has been made to assure the accuracy and applicability of the material contained herein, neither Ontario Hydro nor any person acting on its behalf:

(a) makes any warranty, express or implied with respect to the use of any information, apparatus, method or process disclosed in this report or that such use may not infringe privately owned rights; or

(b) assumes any liabilities with respect to the use of, or for damages resulting from the use of, any information, apparatus, method or process disclosed in this report.

soldiers in the Arctic. A recent report by the IAEA - International Dietary Energy Consulting Group has resulted in a standardization of these methods/2/.

The two isotopes D and ^{18}O are administered separately. Adult studies recommend ideal dose ratios of 0.05 g D_2O/kg of body weight and 0.15 g $H_2{}^{18}O$/kg of body weight /2/. It is important to keep the ratio of the two isotopes close to this ideal level. A typical dose for an adult would be 70 to 80 ml of 10% enriched ^{18}O light water along with the corresponding amount of deuterium isotope in a separate dose of heavy water. However, if the water used for the oxygen isotope dose itself contains a significant amount of deuterium, the matching of the doses becomes impossible.

Oxygen-18 can be produced by the distillation of water. The natural abundance of ^{18}O in water is ≈0.19 atom%. The distillation of water is currently used by the Weismann Institute in their production unit and is the method of choice in a review of separation methods undertaken for the Stable Isotope Research program /4/. However, any water distillation system for oxygen isotopes that produces a high concentration of the oxygen isotope will also concentrate the heavy isotope of hydrogen, resulting in a final product of $D_2{}^{18}O$. In a nutritional study not only must the doses of deuterium and oxygen-18 match the correct ratios, there is the additional concern that the toxicity level for D_2O is 10 atom%. Thus it is necessary to normalize the $D_2{}^{18}O$, i.e. remove the deuterium and substitute hydrogen to form $H_2{}^{18}O$.

There are two potential normalization processes that could be used:

(i) electrolysis of the water, collection of the oxygen gas and then recombination of the gas with a pure hydrogen stream.

(ii) exchange of the water directly with a hydrogen stream over an appropriate catalyst.

2.0 Electrolysis and Recombination

2.1 Process Description

A diagram of this process is given in Figure 1. The first step is electrolysis of the water to produce deuterium gas and oxygen gas. There are two choices for this step; conventional wet electrolyte, electrolysis cells, or the use of a system using a solid polymer electrolyte (the electrolyte provides the conducting H+ ions that are necessary for the electrolysis process to operate).

The second step is the recombination of the oxygen gas with hydrogen. This can be done by burning the oxygen and hydrogen but can be controlled better by using a catalytic recombiner.

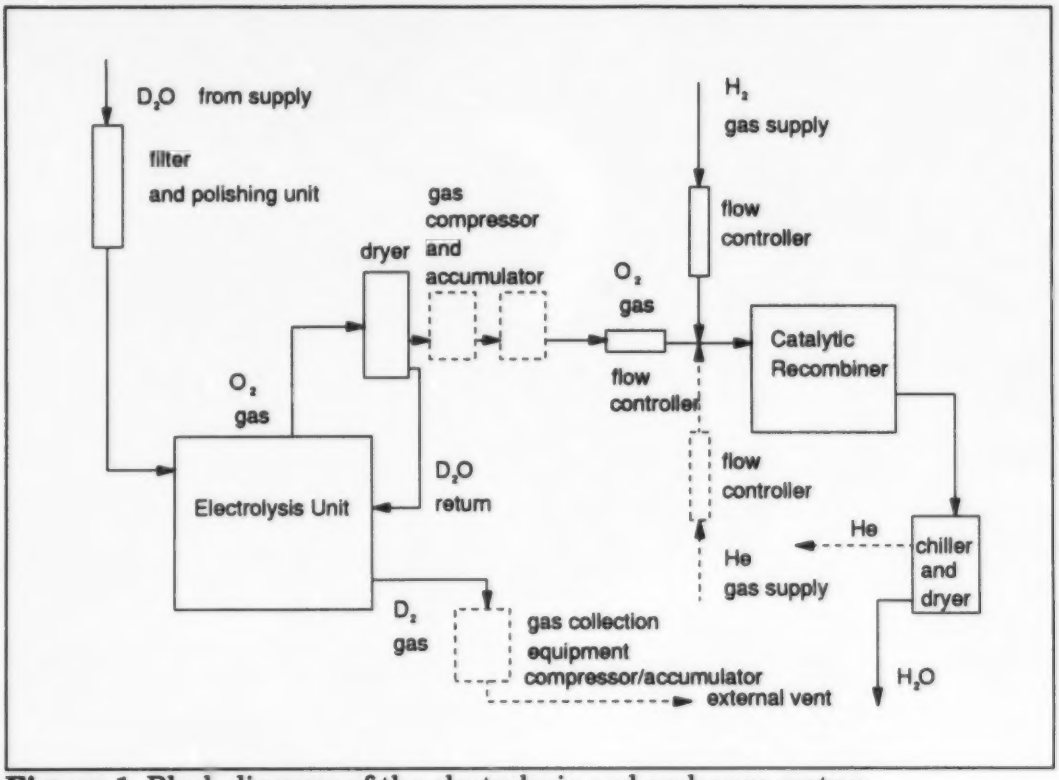

Figure 1. Block diagram of the electrolysis and exchange system.

2.2 Problems with the Process

Conventional electrolysis cells use KOH for the electrolyte (approximately 20% by weight). This is a disadvantage for the production of isotopically pure oxygen gas as the oxygen in the KOH dilutes the product. The alternative is to manufacture KOH from oxygen enriched in ^{18}O or accept the downgrading of the product oxygen for the period of time it will take to equilibrate all the oxygen in the system to the enriched level.

The solid polymer electrolyte systems use a polymer membrane, similar to Teflon, which serves as both electrolyte and separator for product gases. Powdered conductive material, of high catalytic activity, is spread evenly over the membrane and permanently bonded to the membrane face, forming integral electrodes. Conventional cells usually use metallic platinum electrodes. The use of a solid polymer eliminates

the dilution effect of the KOH and the problems associated with handling caustic solutions.[1]

There are large quantities of gas involved in this process. The electrolysis of 10 kg of water will yield 5600 litres (STP) of O_2 gas and 11,200 litres (STP) of D_2. Most electrolysis cells are designed for the production of deuterium or hydrogen gas and the oxygen gas is vented. The cells would have to modified to capture oxygen. Typically oxygen comes off the cells at atmospheric pressure, saturated in water vapour and containing ≈0.4% deuterium gas. This amount of deuterium gas will carry over through the process and will produce ≈250 ppm D in the final light water product.

Electrolysis is an energy intensive process, it requires 0.005 kWhr/litre(STP) of hydrogen gas. This means that 10 kg of water would require 56 kWhr of electricity. An example of an electrolysis system /6/ that produces 4.3 litres(STP)/minute of oxygen gas operates 5 cells at 250 amps using 3 kW of energy.

The oxygen gas must be accumulated and dried in a leak tight system because it is possible to contaminate the oxygen with air. The recombination step has to be handled carefully to prevent stoichiometric mixtures of hydrogen and oxygen from exploding. It may be necessary to dilute the oxygen stream with an inert gas or recombine it with a large excess of hydrogen.

3.0 Countercurrent Exchange

3.1 Process Description

This process is not an immediately obvious way to normalize water. As a background to the process, in 1982 Brookhaven National Laboratory approached Chalk River National Labs requesting information on whether CRNL could convert a large amount of deuterium gas stored at BNL to liquid heavy water (approximately 9.1 million litres of deuterium gas at STP was involved). CRNL's initial concept was to convert the gas to water by catalytic recombination with O_2. A review indicated that a cheaper option was to perform isotopic exchange between the gas and water over the AECL wetproof catalyst /7/.

A unit was designed to perform the exchange reaction:

---

[1] General Electric, Electrochemical Energy Conversion Program was a major industrial user of these types of solid polymer electrolytes. The polymer was manufactured by Hamilton Standard Division. General Electric no longer manufactures these units. Packard Instruments are the only users of this technology now and only in small, bench top units.

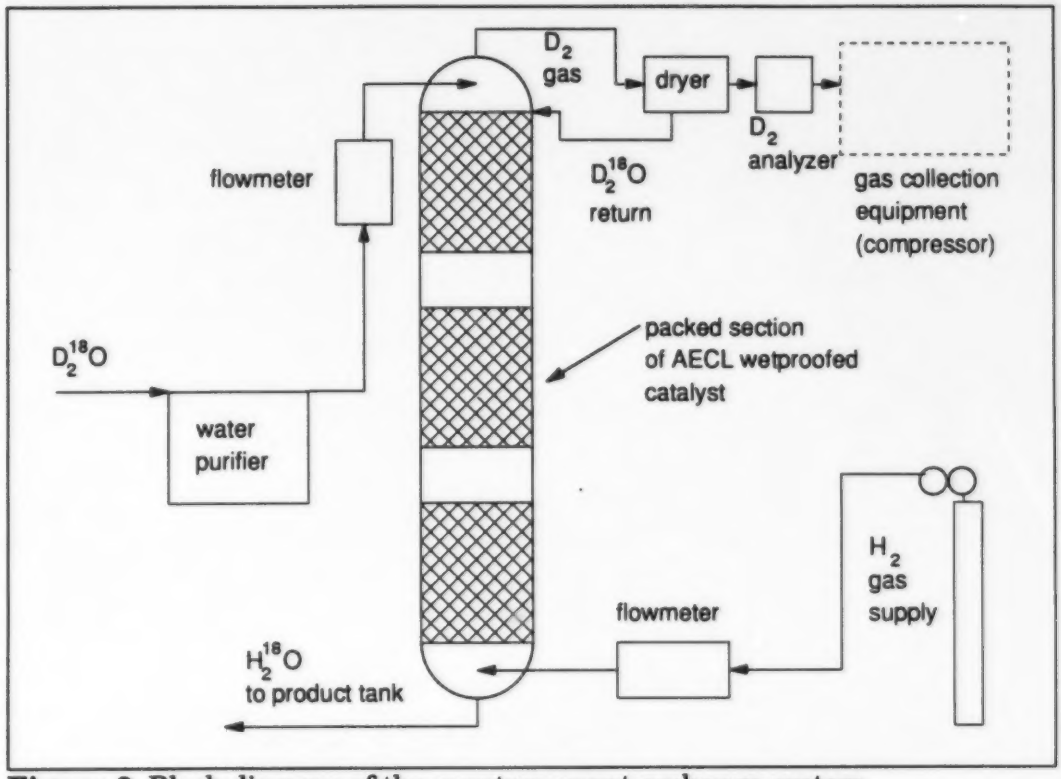

Figure 2. Block diagram of the countercurrent exchange system

$$D_2 + H_2O(liq) \rightleftharpoons D_2O(liq) + H_2$$

Liquid H_2O entered the column at the top and flowed countercurrently to the flow of D_2 gas. A 98% recovery level for the deuterium was established.

A unit was built by CRNL including all the necessary equipment for purification, supply and control of gas and liquid. The exchange column consisted of three flanged lengths of 100 mm diameter (4-in Schedule 10 pipe) packed with an ordered-bed packing-module-type wetproofed isotope exchange catalyst. Total column height was 10m of which 6m was packed with catalyst. Operation began September 1984 and was completed in 15.5 days. During normal operation the deuterium concentration of the effluent gas was <0.1%. The product water averaged 94 wt% D_2O and a total of 7.34 Mg of heavy water was produced. The equipment was built on a metal frame skid and operated outside in an unheated plastic-covered frame structure designed to protect the equipment from inclement weather.

This CRNL experiment corresponds to the reverse of what we wish to do in normalization. It is possible to take this type of unit and run D_2O (liquid) down the

column and H_2 (gas) countercurrently. The D_2 gas generated could be captured at the other end of the column. The process is shown in Figure 2.

3.2 Problems with the Process

It may be necessary to design a different size column because of the different requirements of our exchange. The precise level of D that could be left in the final water would define the column size and dynamics. Removing the D to natural, 148 ppm, levels may be to rigorous a demand for a reasonably sized column. All losses of ^{18}O containing water would have to be examined and a recycle system to capture any water from the gas stream would be necessary.

4.0 Conclusions

The countercurrent exchange system is the recommended system for normalizing heavy water. The advantages are that the capital costs are estimated to be less than building an electrolysis system, because it is technologically simpler and has already been engineered in a large industrial scale. The exchange system has the simplicity of not having to change the state of the isotope of interest from a liquid to a gas and back to a liquid, each stage of which has the potential of isotope losses. Both of these techniques will have to carefully consider the final amount of deuterium that can be present in the product. The production of 148 ppm water will be a challenge for both processes.

Approved:

A.F. Baljet
Manager
Electrical Research Department

Submitted:

J. Robins
Engineer/Scientist
Electrical Research Department

Reviewed:

David L. Mader
for
F. Chu
Section Head
Science Section

References

1. Prentice A.M., "The $^{2}H_{2}{}^{18}O$ Method: New Frontiers in Understanding Human Energy Expenditure", IIS Symposium on Isotope Separation and Applications, Grey Rocks, Quebec, October 11-13, (1990).

2. Prentice A.M. (editor), "The Doubly-labelled Water Method for Measuring Energy Expenditure - Technical Recommendations for Use in Humans - A Consensus Report by the International Dietary Energy Consultancy Group (IDECG) Working Group", IAEA report NAHRES-4, (1990).

3. Jones P., University of British Columbia, private communication.

4. Robins J.R., Bartoszek F.E., "Oxygen Isotope Production Methods, Analysis of Available Techniques", Ontario Hydro Research Division Report No. 91-114K, (1991).

5. Handbury J., "Finishing Unit No. 2 - Oxygen 18 Trial Report, Bruce Heavy Water Plant Report TG-7-90, (1990).

6. Brossard L., Bélanger G., Trudel G., "Performance of a 3-kW (250-A) Electrolyzer", CEA Report No. 031 G 245, (1984).

7. Quaiattini R.J., McGauley M.P., Burns D.L., Tichler P.R., "Conversion of Deuterium Gas to Heavy Water by Catalytic Isotopic Exchange Using Wetproof Catalyst", Nuc. Tech., 77,295 (1987)